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Absence of saturation in the normal-state resistivity of thin films of K_3C_{60} and Rb_3C_{60}

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Crystalline films of C_{60} with ~ 1 μm grain size and a preferred [111] texture have been doped with K and Rb to form superconducting compositions that have sharp zero-resistance transitions. The temperature dependence of the resistance above T_c for both K_3C_{60} and Rb_3C_{60} films reveals metallic behavior up to temperatures as high as 520 K without any evidence of saturation. For Rb_3C_{60}, electronic mean free paths significantly shorter than nearest-neighbor C_{60} distances and anomalously high values of the electron-phonon coupling strength are inferred. These results suggest that there is a strong interaction between the conduction electrons and the intramolecular vibrational modes and also bring into question the assumption that all of the donated charge (three electrons per C_{60}) is itinerant.

The discovery of conductivity[1] and superconductivity[2] in the alkali-metal-doped fullerenes has prompted numerous investigations of the properties of these most unusual materials. Although there has been significant progress in the fabrication of high-quality samples of bulk powders and single crystals, work with thin films has been somewhat slowed by processing difficulties. These difficulties are due in part to the extreme air sensitivity of the doped materials, a problem exacerbated by the large surface area of thin films, and in part to the small grain size and associated granular morphology. Transport measurements made with such granular films[2,3] reveal broad superconducting transitions with reduced T_c and also do not show the metallic (positive temperature coefficient of resistance) behavior exhibited by crystals.[4,5]

In this paper we report the use of a thermal-gradient technique to grow polycrystalline C_{60} thin films comprising face-centered-cubic grains approximately 1 μm in size and having a preferred [111] texture. The vapor phase doping with alkali metals is accomplished in evacuated glass tubes containing solid-state alkali-metal dispensers, miniature sorption pumps to remove contamination, and electrical connections for transport measurements. When optimally doped to a stoichiometry of three alkali atoms per C_{60},[6,7] the K_3C_{60} and Rb_3C_{60} samples exhibit pronounced resistance transitions to the superconducting state and have a metallic temperature dependence to the resistivity, ρ. This metallic dependence extends to temperatures as high as 520 K without showing any evidence of saturation or leveling off. Absence of a tendency towards saturation[8] normally implies that over the entire temperature range the mean free path is longer than the nearest-neighbor spacing between scattering centers. For the case of Rb_3C_{60} with $\rho(520\ \mathrm{K})=5.5$ mΩ cm, we calculate using elementary Bloch-Boltzmann analysis a transport scattering length, $l_{tr}=0.63$ Å. This length is significantly shorter than the 10 Å distance separating adjacent C_{60} molecules. Also, from the linear temperature dependence of the high-temperature resistivity and the measured plasma frequency, ω_p,[9] we obtain an estimate, $\lambda_{tr}=4.4$, of the transport electron-phonon coupling constant. Strong coupling and short mean free paths are self-consistent but not compatible with a metallic temperature dependence. Accordingly, these unusual normal-state properties, i.e., an unphysically short mean free path, an anomalously high λ_{tr}, and a metallic dependence to the resistivity showing no sign of saturation, imply that a conventional Bloch-Boltzmann analysis is inadequate to describe electronic transport in the alkali-metal-doped fullerenes. In the absence of alternative and perhaps novel mechanisms for transport in these unusual materials, our results enforce a critical assessment of the experimental assumptions underlying such an analysis.

The crystalline C_{60} films described in this study were grown using sublimation in a gradient furnace in a manner similar to that reported for growing single crystals[10] and textured films on mica.[11] An evacuated quartz tube is placed into a furnace having two temperature zones, a hot (~ 400 °C) central zone for the sublimation of C_{60} and a cooler (~ 200 °C) end zone for placement of the substrate onto which C_{60} vapor is condensed. The absolute value of the temperatures and the relative temperature differences between the hot and cold zones of the furnace determine the morphology and grain size of the films. Typical 5000-Å-thick films are grown in approximately 12 hours in a dynamic vacuum of 6.0×10^{-7} Torr. In contrast to the smooth and specular granular films grown by vapor sublimation onto room-temperature substrates,[2,3,7] these vapor-transport films have a rough diffuse appearance due to faceted grains approximately 1 μm in size.

X-ray diffraction data from a typical "crystalline" C_{60} film deposited onto a glass substrate are shown in Fig. 1. The x-ray peak widths are limited by the resolution of the diffractometer ($\sim 0.25°$ 2θ). This suggests that the structural coherence of these films may approach that seen in sublimed crystals (>5000 Å). The long-range order seen in these films can be contrasted with the short structural coherence length (<100 Å) seen in "smooth" C_{60} films and bulk powder samples. The crystalline films have nearly complete [111] texture as indicated in Fig. 1 by the weak (220) and (311) peaks. The (311) peak is about 2% of the intensity expected if the film has ran-

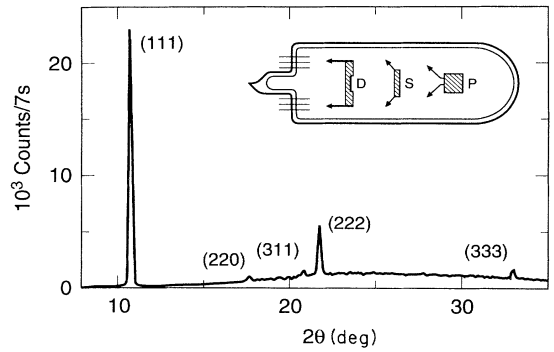

FIG. 1. X-ray diffraction scan of a 1600-Å-thick crystalline film deposited on a glass substrate and showing predominantly [111] texture. The inset depicts schematically the glass doping apparatus containing the alkali metal dispenser (D), the porous getter pump (P), and the C_{60}-coated substrate (S).

domly oriented polycrystalline grains. Scans of off-axis peaks indicate that the films have only planar order with no in-plane orientational order. The diffuse background in Fig. 1 is from the glass substrate.

Shown in the Fig. 1 inset is a schematic of a glass-enclosed assembly used for alkali-metal doping and subsequent measurement of transport properties. Platinum leads epoxied in a Van der Pauw configuration to Ag pads on the C_{60}-coated substrate serve the dual role of supporting the sample while providing a means to monitor the sample resistivity. The alkali-metal dispenser, D, and porous getter,[12] P, are outgassed (by applying electric currents) in vacuum before backfilling the assembly with He to a pressure of 0.10 Torr and then flame sealing the pump-out tube. This pressure is sufficient to provide some thermal coupling to the sample and yet low enough to allow a reasonable flux of A metals (A=K,Rb) to reach S from D. Doping is accomplished by placing the entire assembly in an oven set for temperatures in the range 150–250 °C and then alternately exposing the sample to a flux from D followed by an anneal. It is important not to overdope the sample past the resistance minimum[7] ($x=3$ for A_xC_{60}) since the tube assemblies cannot tolerate the 400 °C temperatures that are required[13] to form A_3C_{60} (e.g., $K_6C_{60}+C_{60}\rightarrow 2K_3C_{60}$) when the insulating A_4C_{60} or A_6C_{60} phases are present due to overdoping. Because of slow A atom diffusion and the necessity of avoiding an overshoot of the resistivity minimum, the length of time to reach the resistance minimum after a succession of expose-anneal cycles is typically one week.

There are significant differences in transport properties between these doped crystalline films described here and the granular films reported previously.[2,3,7] First, the temperature dependence of the resistance, as shown in Fig. 2 for a 5100-Å-thick Rb_3C_{60} film, is metallic, having sharp superconducting transitions and zero resistance at the bulk value. In constrast, the temperature-dependent resistivity of granular films is nonmetallic with broad superconducting transitions and suppressed T_c's. Another significant difference appears in the doping dependence of ρ shown in Fig. 3. Here the resistivity of a 3910-Å-thick

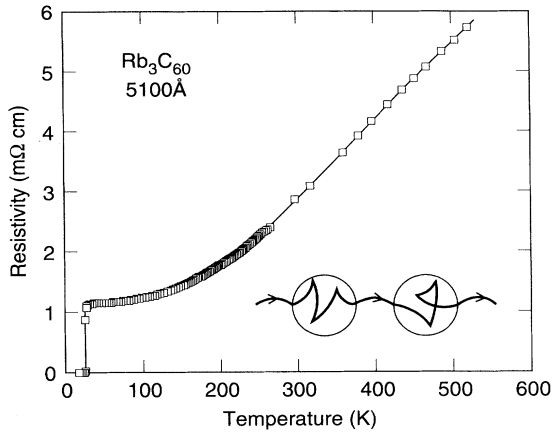

FIG. 2. Plot of resistivity as a function of temperature for a 5100-Å-thick crystalline Rb_3C_{60} film. The inset depicts schematically electronic transport where the charge carriers are confined predominantly on individual molecules.

K_xC_{60} film that had been doped to its resistance minimum ($x=3$ at origin) was monitored during exposure to a constant flux of K atoms. The resistance increases with doping, showing a shoulder at $x=4$ and a pronounced increase towards infinity at $x=6$. This shoulder at $x=4$ is indicative of a bct K_4C_{60} phase that has been identified in bulk powders[14] but not seen previously in films. Beyond $x=6$, additional K atoms cannot be accommodated in the host C_{60} lattice and therefore precipitate out on the surface with an equilibrium thickness determined by the oven temperature and the rate of arrival of K atoms from the dispenser.

One of the more striking aspects of the data for Rb_3C_{60} in Fig. 2 is the linear temperature dependence of the resistivity above room temperature. Shown in Fig. 4 is a resistivity plot of this high-temperature region for a K_3C_{60} film and two Rb_3C_{60} films with different thicknesses. These data are reproducible and do not show hysteresis with temperature cycling between room temperature and 520 K. The maximum temperature of

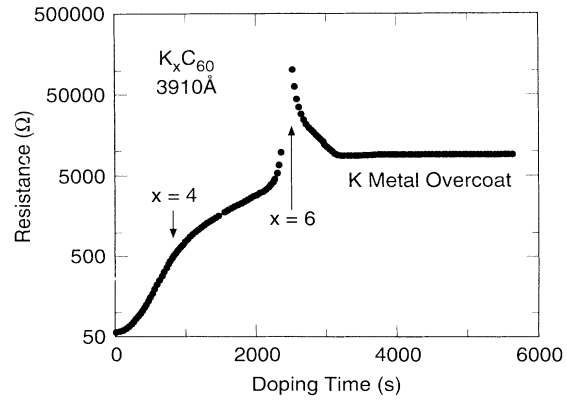

FIG. 3. Resistance on a logarithmic scale as a function of doping time for a 3910-Å-thick crystalline K_3C_{60} film. The film had been previously doped to its resistance minimum near 50 Ω. The shoulder at $x=4$ indicates the presence of K_4C_{60} and the cusp at $x=6$ is the fully doped K_6C_{60} phase.

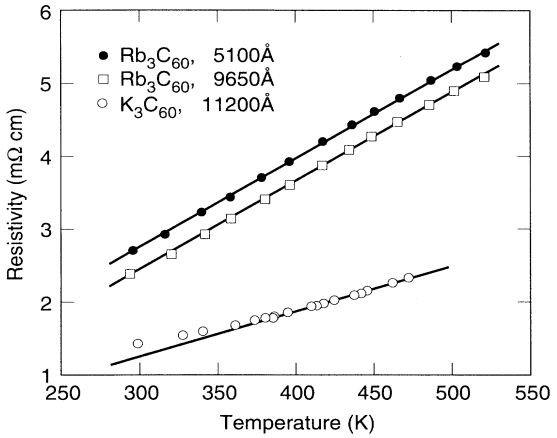

FIG. 4. High-temperature resistivity data for one K_3C_{60} film and two Rb_3C_{60} films having thicknesses indicated in the legend.

520 K is evidently not high enough to cause irreversible out diffusion of alkali metal. The resistivity and resistivity slopes for Rb_3C_{60} appear to be intrinsic since the data for the two films with almost a factor of two difference in thickness almost overlap.

One criterion for the validity of a Bloch-Boltzmann analysis, which we now apply to these data, is that the carriers can be represented as quasiparticles in a periodic potential. For three electrons donated into the triply-degenerate t_{1u} band of each C_{60} molecule, it is straightforward to calculate in a spherical Fermi-surface approximation, the Fermi wave vector, $k_F=(\pi^2 n)^{1/3}$, where $n=4.1\times10^{21}$ cm^{-3} is the volume charge density and a factor of 3 has been included to account for orbital degeneracy. The conductivities, $\sigma_\alpha=n_\alpha e^2\tau/m$, of each of the three bands add in parallel to give the standard Drude result, $\sigma=ne^2\tau/m$, where $n_\alpha=n/3$ is the carrier density in each band, τ is a scattering time, and m is the band mass. Using the standard conversion, $\tau/m=l_{\rm tr}/\hbar k_F$, and the relation between n and k_F derived above, we find the result for the mean free path,

$$l_{\rm tr}=\pi^2(\hbar/e^2)/\rho k_F^2 , \quad (1)$$

in terms of k_F and the resistivity, $\rho=1/\sigma$. The resulting $l_{\rm tr}=0.63$ Å calculated for $\rho=5.5$ mΩ cm is significantly shorter than both the 10 Å nearest-neighbor distance between C_{60} molecules and the average separation, $n^{-1/3}=6$ Å, between conduction electrons. A more relevant length scale appears to be the 1.4 Å distance between C atoms on each C_{60} molecule; although these atoms, because of rotational disorder, cannot be used to form a periodic potential in which Bloch waves can propagate.

An additional parameter, the transport electron-phonon coupling constant, $\lambda_{\rm tr}$, can be estimated from the relation,[15]

$$\lambda_{\rm tr}=0.24(\hbar\omega_p)^2\alpha , \quad (2)$$

where ω_p is the bare plasma frequency (eV) and α the resistivity slope (mΩ cm K^{-1}). This relation derives from the Drude expression, $\rho=4\pi/\omega_p^2\tau$, and the fact that the scattering by phonons (or other bosonic excitations) has a rate, τ^{-1}, linear in T and proportional to $\lambda_{\rm tr}$ for temperatures, T, above a characteristic energy scale of the phonon. For Rb_3C_{60} the experimental value, $\omega_p=1.2$ eV, determined from infrared reflectance,[9] and $\alpha=12.2$ μΩ cm K^{-1}, determined from the slopes in Fig. 4, give the result, $\lambda_{\rm tr}=4.4$. We note that the high-temperature slope of $\rho(T)$ does not extrapolate to the residual resistivity, ρ_0, as it would in classical Bloch-Gruneisen behavior, and that therefore the real $\lambda_{\rm tr}$ will be somewhat smaller.

These two results, a short $l_{\rm tr}$ and a strong electron-phonon coupling, imply that an electron is for the most part confined to the surface of a given molecule and therefore is able to interact strongly with the *intramolecular* phonons before hopping to the next molecule. This behavior is represented schematically in the inset of Fig. 2.

We now examine more closely the experimental assumptions that have led us to suspect the applicability of Bloch-Boltzmann theory. The first of these centers on the question as to whether the measured resistivities are intrinsic. Infrared reflection data extrapolated to zero frequency[16] imply a residual resistivity, $\rho_0=0.4$ mΩ cm, approximately a factor of three lower than the value shown in Fig. 2. Using this "optical" value in Eq. (1), we compute the low-temperature normal-state value, $l_{\rm tr}=8.7$ Å, a scattering length still less than the nearest-neighbor C_{60} distance. Assuming a similar resistivity ratio of approximately 5 as shown in Fig. 2, $l_{\rm tr}$ at high temperatures would be reduced to 1.7 Å. We note that the temperature dependence (below 250 K) and the ρ_0's of the best Rb_3C_{60} crystals reported to date[17] are similar to those reported here. Accordingly, it is difficult to imagine that improved processing procedures will be capable of producing films or crystals with resistivities significantly smaller than achieved at present when only a factor of approximately three improvement with respect to the originally reported granular films[2,3,7] has currently been obtained.

A second consideration, which has also been used to explain temperature dependence in nuclear-magnetic spin-relaxation data on K_3C_{60} and Rb_3C_{60},[18] is the role of thermal expansion. To avoid such effects, resistivity measurements should be made at constant volume[19] rather than constant pressure as has been done in our experiment. We can estimate, however, the magnitude of thermal expansion effects with the following argument. Measurements of the density of states at the Fermi energy, $N(E_F)$, by NMR (Ref. 18) and magnetic susceptibility[20] have shown that $N(E_F)$ for Rb_3C_{60} with a lattice constant $a=14.43$ Å and $T_c=29$ K is $\sim$ 30% larger than for K_3C_{60} ($a=14.24$ Å and $T_c=29$ K). Since $N(E_F)=m^*k_F/\hbar^2\pi^2$ and k_F is roughly the same for the two compounds, then $m^*_{Rb_3C_{60}}\approx1.3m^*_{K_3C_{60}}$, where m^* is the effective band mass. The experimentally determined approximately linear relation[21] between T_c and a thus allows a calibration, $\delta m^*/m^*=0.3$ for a lattice change $\delta a=14.43-14.24=0.19$ Å. Using the isobaric thermal-expansion coefficient,[22] $\lambda(\ln a)/T=3.1\times10^{-5}$ K^{-1}, the expected expansion of the Rb_3C_{60} lattice in the

temperature range $300\,°C \leq T \leq 500\,°C$ is 0.09 Å. Assuming that the scattering rate τ^{-1} is independent of $N(E_F)$, and since $\rho = m^*/ne^2\tau$, we can now estimate that thermal-expansion effects in the linear range above room temperature give rise to a $\delta\rho/\rho = 0.3(0.09/0.19) = 0.14$. Accordingly, to first order we might expect such a modest effect to increase the resistivity slope by 14% and not change the curvature (i.e., convert a dependence which has a negative curvature due to an approach towards saturation to a dependence which is linear). If there is a dependence of τ^{-1} on $N(E_F)$, say, $\tau^{-1} \propto N(E_F)$, then our estimate of $\delta\rho/\rho$ increases by a factor of two to 28%. This is a moderate perturbation on the more than a factor of two increase observed in the data of Fig. 4.

A third and final assumption that needs to be questioned is the use of three electrons per C_{60} molecule in the calculation of k_F. Raman[1] and stoichiometry[6,7] measurements together imply that all of the A atoms in A_3C_{60} have fully donated their valence electrons into the t_{1u} conduction band of C_{60}. It may be, however, that some fraction of the donated charge is pinned by a charge-density wave so that the amount of itinerant charge is lower than three per C_{60}.[23] A lower n and a correspondingly larger l_{tr} would then be compatible with a Bloch-Boltzmann explanation for the high metallic resistivities. Tentative experimental support for a lower n can be found in optical reflection data for Rb_3C_{60} in which the response is assumed to arise from two contributions: a Drude plasma edge at significantly lower energy than reported in Ref. 9 and a midinfrared excitation of unknown origin at higher energy.[24] A lower plasma frequency reduces the value of λ_{tr} calculated from Eq. (2) and can arise from either a large effective mass or reduced itinerant electron density.

If the resistivities reported here are close to intrinsic, if thermal-expansion effects do not severely mask a tendency towards saturation, and if the three electrons donated to each C_{60} molecule are itinerant, then alternative mechanisms for transport must be considered. Relevant theories should include the effect of orientational disorder[25] and should also treat the charge carriers as being confined to each molecule for a significant fraction of the time, as shown schematically in the inset of Fig. 2. The temperature dependence in such a picture derives from the interaction of electrons with thermally excited localized excitations (intramolecular vibrations), a situation unique to the alkali-metal-doped fullerenes in which each scattering center (a C_{60} molecule) possesses numerous (174 for C_{60}) internal degrees of freedom. An interesting way to think of conduction in this limit is by analogy to resonant tunneling in which thermal excitations on each scattering center give rise to a mismatch of levels affecting each electron tunneling "through" the C_{60} molecules and hence a decreased transmission probability or increased resistance as the temperature is raised. It is by no means clear that such a mechanism leads to a linear $\rho(T)$ dependence.

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